Macromolecules

Article

pubs.acs.org/Macromolecules

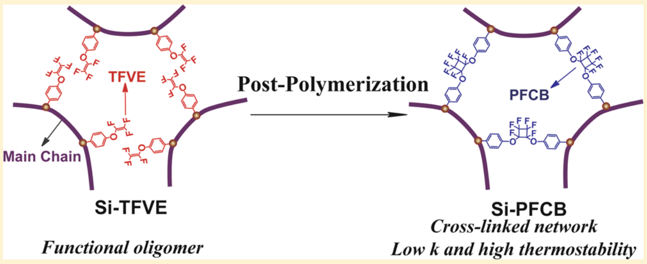
Postpolymerization of Functional Organosiloxanes: An Efficient Strategy for Preparation of Low-*k* Material with Enhanced Thermostability and Mechanical Properties

Chao Yuan,[†] Jiajia Wang,[†] Kaikai Jin, Shen Diao, Jing Sun, Jiawei Tong, and Qiang Fang*

Key Laboratory of Synthetic and Self-Assembly Chemistry for Organic Functional Molecules, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, People's Republic of China

Supporting Information

ABSTRACT: A novel functional oligomer (**Si-TFVE**) with a siloxane backbone and thermally cross-linkable trifluorovinyl ether groups ($-OCF{=}CF_2$) is reported here. When postpolymerized at high temperature, **Si-TFVE** converts to an amorphous cross-linked network (**Si-PFCB**), which shows a dielectric constant of 2.33 and dielectric loss below 2.1×10^{-3} at 30 MHz. **Si-PFCB** also shows excellent film uniformity with the surface roughness less than 5.79 nm over a 1 μm square area. Moreover, **Si-PFCB** shows high thermostability with a 5 wt % loss temperature of 472 °C and no obvious T_g below 350 °C. In regard to the mechanical properties, **Si-PFCB** has Young's modulus, hardness, and bonding strength with silicon wafer surface of 10.06 GPa, 0.392, and 4.93 GPa, respectively. These results suggest that such oligomer is suitable for utilization in ultralarge scale integration circuits. In addition, this contribution provides a new route to prepare cross-linked organosiloxanes only by heating instead of using catalysts or initiators in the traditional procedures.



INTRODUCTION

In the microelectronic industry, low dielectric constant (low-*k*) materials are crucially needed to reduce the resistance-capacitance (RC) delay and cross-talk in integrated circuits (IC).[1−6] Therefore, great efforts have been made in search of novel low-*k* materials in the past decades. Inorganic and organic siloxanes[7,8] as well as organic polymers[9−15] have been recognized as the preferable candidates for interlayer dielectric (ILD) materials. However, only few of them are compatible with the back-end-of-the-line (BEOL) production procedures.[2,4] For example, the insulators derived from silicon dioxide exhibit nonideal dielectric performance, while organic polymers usually show disqualified thermostability, anisotropy of dielectric, inferior adhesion strength, and relatively low glass transition temperature (T_g).[9−15] Thus, to improve the above-mentioned situation two strategies have been developed. One is to introduce pores with favorable size and distribution,[4,16,17] and the other is to use the least polarizable bonds such as C−F bond in molecular design. Nevertheless, precise control of pores' generation and efficient molecular design still remain a big challenge.[16−18] To improve the thermostability and mechanical properties, dense cross-linkable groups are introduced into the side chains of the polymers.[19] However, in many cases, the modified polymers show unsatisfactory *k* values.

On the basis of the high thermostability and good adhesion properties of siloxanes and the low-*k* values of fluoropolymers, we synthesized a new oligomer (trifluorovinylether-functionalized siloxanes (**Si-TFVE**)) with a siloxane backbone and cross-linkable trifluorovinylether ($-OCF{=}CF_2$) side chains (Scheme 1). **Si-TFVE** showed good film forming capacity, and the film prepared from spin-coating was treated at high temperature to produce a cured network, which exhibited a *k* value of 2.33 at 30 MHz with a dielectric loss less than 2.1×10^{-3}. Moreover, the cured **Si-TFVE** showed high thermostability and good mechanical properties, suggesting that it could meet the requirements of Cu damascene metallization. It is worth emphasizing that the cross-linking of organosiloxanes usually requires catalysts or initiators (platinum or peroxides),[20] while in our case the cross-linking occurs by only heating, indicating that this contribution provides a new route to form cross-linked organosiloxanes and is of considerable industrial importance.

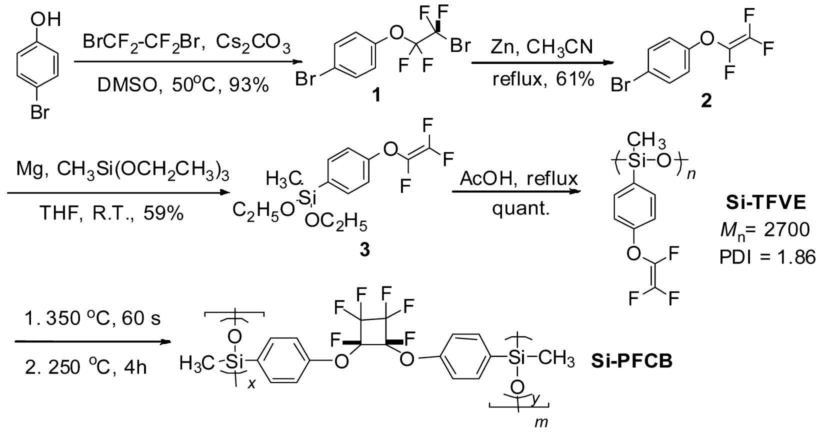
EXPERIMENTAL SECTION

Reagents and Instruments. All starting materials were purchased from Aldrich and Acros companies and used without further purification. All solvents were dehydrated and distilled under an inert atmosphere before use. ^{1}H and ^{13}C NMR spectra were recorded on Bruker DRX 400 or Varian mercury 300 spectrometer using $CDCl_3$ as solvent and TMS as internal standard.

Synthesis. Synthesis of compounds **1**, **2**, and **3** (see Scheme 1): these compounds were prepared according to the previously reported procedures.[21−23]

Received: June 18, 2014
Revised: August 20, 2014
Published: September 4, 2014

Scheme 1. Procedures for the Synthesis of Si-TFVE and Si-PFCB



Synthesis of oligomer **Si-TFVE**: a solution of **3** (18.38 g, 60 mmol) in acetic acid (36 g, 0.6 mol) was refluxed with vigorous stirring for 24 h. After being cooled to room temperature, the mixture was evaporated under vacuum. **Si-TFVE** was obtained in a yield of 99%. M_n = 2700 and polydispersity (PDI) = 1.86. ^{1}H NMR (400 MHz, CDCl$_3$), δ (TMS, ppm): 7.74−7.14 (m, 2H), 7.13−6.71 (d, 2H), 0.57−0.18 (m, 3H). 19F NMR (376 MHz, CDCl$_3$), (TMS, ppm): −134.1∼−134.3 (m, 1F), −126.2∼−126.8 (m, 1F), −119.3∼−119.8 (m, 1F).

Devices Fabrication and Measurement of Dielectric Properties. Preparation of **Si-PFCB** film and measurement of dielectric properties: a solution of **Si-TFVE** in toluene was spin-coated on an aluminum-backed silicon wafer (heavily doped single crystal silicon with a resistivity of 3.5 × 10^{-3} Ω.cm) to form a sticky film.

The wafer was quickly placed on a hot-plate, which was preheated to 350 °C. After being maintained at the temperature for 60 s, the wafer was moved to an oven and heated at 250 °C for an additional 4 h under nitrogen. Thus, the fully cured **Si-PFCB** film was obtained. The thickness of **Si-PFCB** film was measured by field emission scanning electron microscopy (FE-SEM). For measurement of the dielectric properties of the film, aluminum was then deposited on the surface of the film via vacuum evaporation as a top electrode (the diameter = 3.54 mm). A parallel plate capacitor was thereby fabricated. The dielectric properties of the film were measured from an Agilent 4294A precision impedance analyzer at room temperature, and the data were processed according to the previously reported method.[9]

■ RESULTS AND DISCUSSION

As shown in Scheme 1, **Si-TFVE** was obtained in a quantitive yield by hydrolysis of precursor **3** in acetic acid.[24] Analysis by GPC (polystyrene standards) showed that **Si-TFVE** had number-average molecular weight (M_n) and polydispersity index (PDI) values of 2700 and 1.86, respectively. According to the M_n, the number of the repeating unit of **Si-TFVE** was estimated at about 12. It was noted that the hydrolysis of siloxanes in the presence of acetic acid usually gave a mixture of linear and cyclic products.[24] Such a phenomenon was also observed in our case, whereas the linear products were dominant. As can be seen from a curve of GPC of **Si-TFVE** (see Supporting Information, Figure S1), the ratio between **Si-TFVE** and the cyclic products was estimated as about 93:7. The molecular weight of Si-TFVE was also confirmed by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS), as shown in Supporting Information (Figure S2).

Si-TFVE was easily soluble in common solvents such as chloroform, toluene, and tetrahydrofuran. It was interesting that the film on the wafer was in a sticky liquid rather than a solid state after spin-coating. Accordingly, the flattening of the surface was easily achieved, and the microgaps could be conveniently filled.

Thermal cross-linking (or curing) behavior of **Si-TFVE** was evaluated by differential scanning calorimetry (DSC). As depicted in Figure 1, the curing started at about 155 °C and the peak was at 241 °C. Such curing behavior of **Si-TFVE** was similar to that of the polymers containing −OCF═CF$_2$ groups,[25,26] indicating that the thermal cross-linking of **Si-TFVE** was only motivated by the [2 + 2] cyclodimerization reaction of −OCF═CF$_2$ rather than the reaction between silanols.

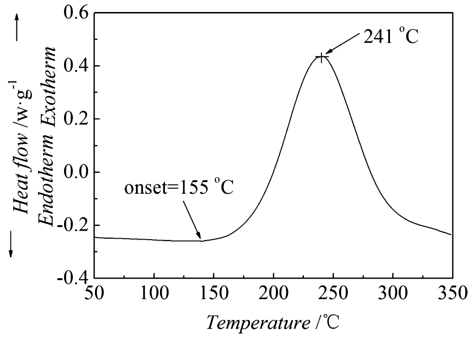


Figure 1. DSC traces of **Si-TFVE** under N$_2$ with a heating rate of 10 °C/min.

According to the DSC traces, we tried to prepare the cured **Si-TFVE** (called as **Si-PFCB**) film for the measurement of dielectric and mechanical properties. It was noted that most of the thermosetting resins such as epoxy and phenolics resins tended to shrink during curing, which were unbeneficial to prepare films of high quality. In our case, irregular shrinking was also observed when the curing ran for long time at 160 and 250 °C, respectively (near its onset and peak exothermic temperatures in DSC, see Figure 1). Through many trials, we finally found that the curing at a much higher temperature (350 °C) within a short period (60 s) can efficiently restrain the shrinking and extremely smooth film was thus obtained.

A comparison of **Si-TFVE** with **Si-PFCB** in FT-IR spectra was depicted in Figure. 2. After curing, the −OCF═CF$_2$ stretching vibration peak at 1739 cm^{-1} disappeared in **Si-TFVE**, and a new perfluorocyclobutyl peak appeared at 962 cm^{-1} in **Si-PFCB**.[26b] This meant that **Si-TFVE** had completely converted to **Si-PFCB**.

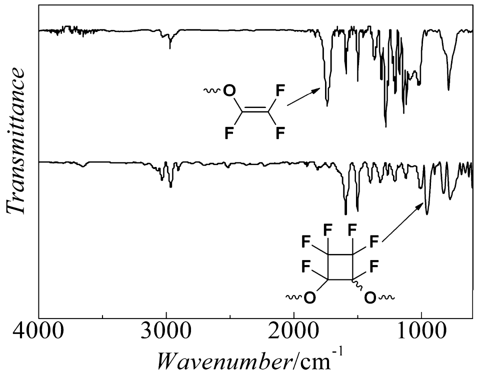


Figure 2. FT-IR spectra of **Si-TFVE** (up) and **Si-PFCB** (down).

In order to well understand the formation of **Si-PFCB**, a schematic description was made. As shown in Figure 3, the thermoplastic Si-TFVE turned into thermoset Si-PFCB upon heating without any additives.

The dielectric constants of **Si-PFCB** films were measured by the capacitance method,[9] and the detailed procedures are described in the Experimental Section. The thickness of the film was determined by field emission scanning electron microscopy (FE-SEM). Figure 4 shows an FE-SEM micrograph of the section plane of a **Si-PFCB** film on a silicon wafer. Obviously, the **Si-PFCB** film possesses good surface uniformity. The dielectric constant (k) and dielectric loss (tan δ) of the film are depicted Figure 5. As expected, the average k value of **Si-PFCB** film keeps below 2.45 with a dielectric loss below 2.1 $\times$ 10^{-3} in a range of frequencies varying from 1 to 30 MHz. Moreover, the dielectric value is only 2.33 at 30 MHz, which is much lower than those of most widely used low-k materials,[7−18] such as polyimides, polycyanate esters, and SiLK resins.

This is mainly due to the existence of fluorous groups showing large free volume and low capacity to be polarized.[2] On the other hand, X-ray diffraction (XRD) patterns (Figure 6) demonstrate that the **Si-PFCB** film is essentially amorphous and molecular stacking is avoided. The peak at 2θ = 13.8° (d = 0.64 nm) is assigned to the interlayer distance of **Si-PFCB**. Such large interlayer distance implies that **Si-PFCB** emerges as an untight stacking structure in the solid state, resulting in low density. On account of the above-mentioned characteristics, **Si-PFCB** thereby exhibits low-k value.

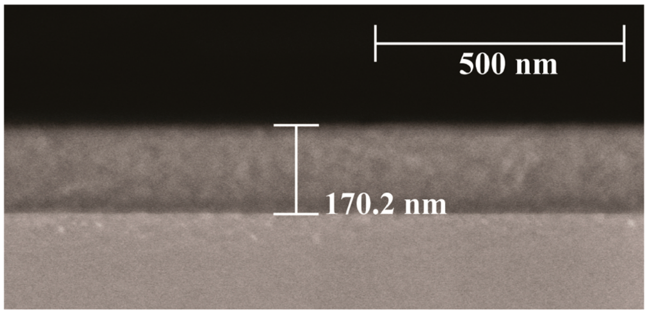


Figure 4. A field emission scanning electron microscopy image of a **Si-PFCB** film.

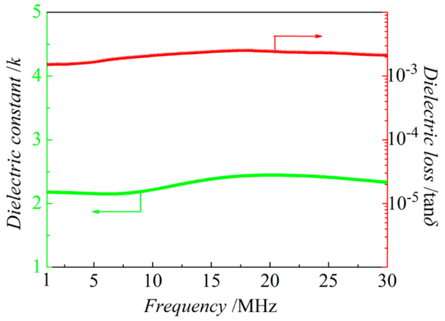


Figure 5. Dielectric constant and dielectric loss of a **Si-PFCB** film at different frequencies at room temperature.

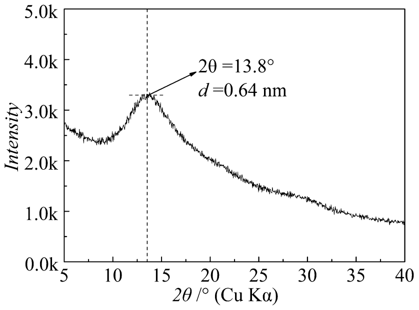


Figure 6. XRD patterns of **Si-PFCB** film.

The thermostability of **Si-PFCB** was evaluated by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). DSC trace indicated no evidence of glass transition in a range of temperatures from 50 to 350 °C (Figure 7, see attached chart), demonstrating the good thermostability of **Si-PFCB**. Such high thermostability was also supported by TGA results (Figure 7) in which **Si-PFCB** showed the 5 wt % loss temperature of 472 °C. From the view of application, the heat

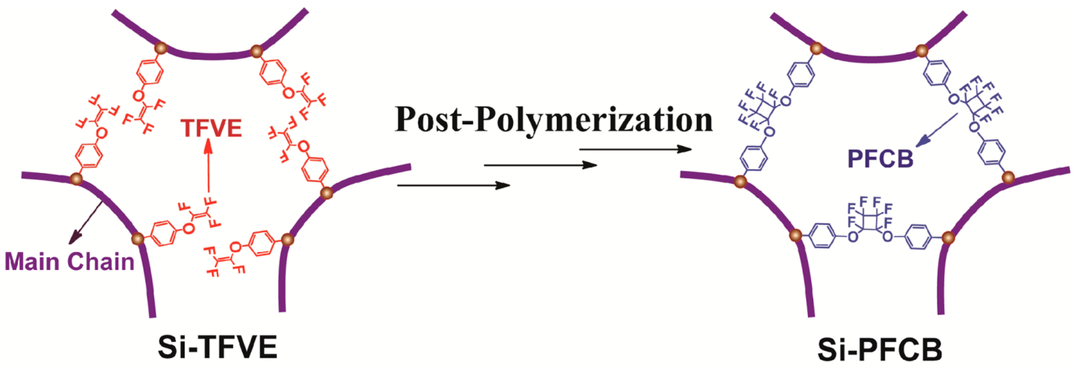


Figure 3. A schematic description for the formation of **Si-PFCB** via heating **Si-TFVE**.

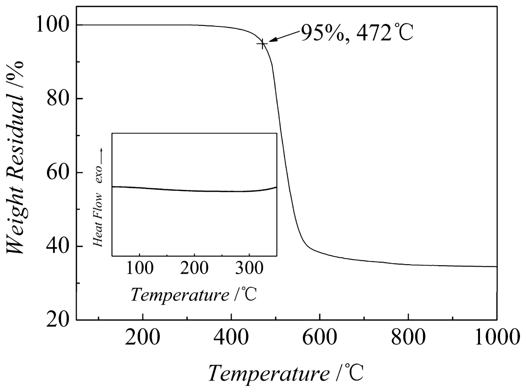


Figure 7. TGA curve of **Si-PFCB** under N_2 with a heating rate of 10 °C/min. The attached chart is DSC trace of **Si-PFCB**.

resistance of **Si-PFCB** could meet the requirements for the fabrication of Cu metallization during the damascene processes.[2,4]

The hydrophobicity of **Si-PFCB** films was evaluated by water contact angle test. On the surface of the film, water contact angle was measured as 105 ° (Figure 8), exhibiting good hydrophobicity of the film. Thus, moisture absorbance, which results in deterioration of the dielectric properties, could be effectively prevented.

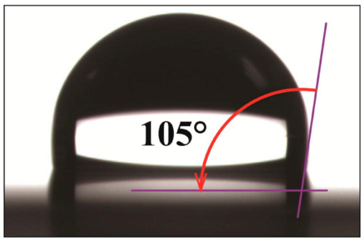


Figure 8. Contact angle of water on the surface of a **Si-PFCB** film.

The mechanical properties of **Si-PFCB** film were determined from a nanoindentation/scratch system. The results showed that the film had an average hardness of 0.392 GPa and a Young's modulus of 10.06 GPa (Figure 9). The bonding strength between the film and a silicon wafer was measured as 4.93 GPa, which also satisfied the BEOL procedures.[2,4]

Film uniformity is crucial to the production of a low-*k* material as well. As can be seen from Figure 4, the cross-section picture from the FE-SEM manifests the **Si-PFCB** film spin-coated on a silicon wafer has a smooth surface. Furthermore, this is verified by atomic force microscopy (AFM) with both a planar graph and a stereogram from an angle of 45 ° (Figure 10). Over a 1 μm square area, the surface roughness was less than 5.79 nm, which satisfied the demand of thickness lower than 10% within the wafer.[10]

■ CONCLUSIONS

In summary, based on the high heat resistance of organosiloxanes and the good dielectric properties of fluoropolymers, we successfully prepared a novel oligomer with a siloxane backbone and thermocurable trifluorovinylether ($-OCF=CF_2$) side chains. Upon postpolymerization, the oligomer converted to a cross-linked network (**Si-PFCB**), which showed high thermostability and good dielectric properties with an average dielectric constant below 2.45 and a dielectric loss less than 2.1×10^{-3} in a range of frequencies varying from 1 to 30 MHz. In addition, the **Si-PFCB** film exhibited excellent surface smoothness and good hydrophobicity. The mechanical properties of **Si-PFCB** were also satisfactory with Young's modulus, hardness, and bonding strength with silicon wafer surface of 10.06 GPa, 0.392, and 4.93 GPa, respectively. These data indicated that the oligomer was suitable for utilization in ultralarge scale integration circuits. Moreover, this article also

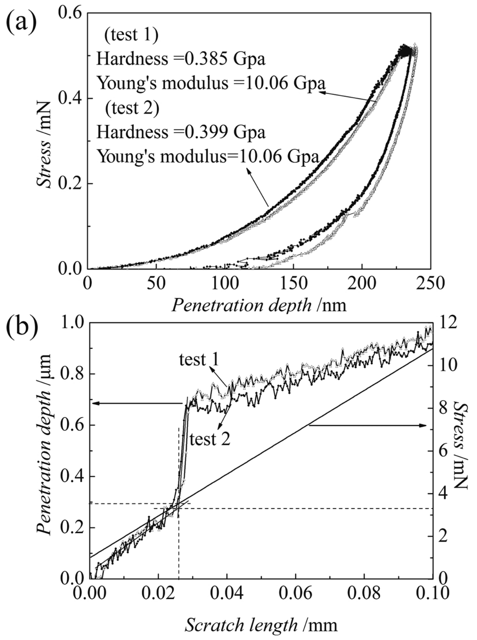


Figure 9. Results from nanoindentation (a) and nanoscratch (b) tests for a **Si-PFCB** film.

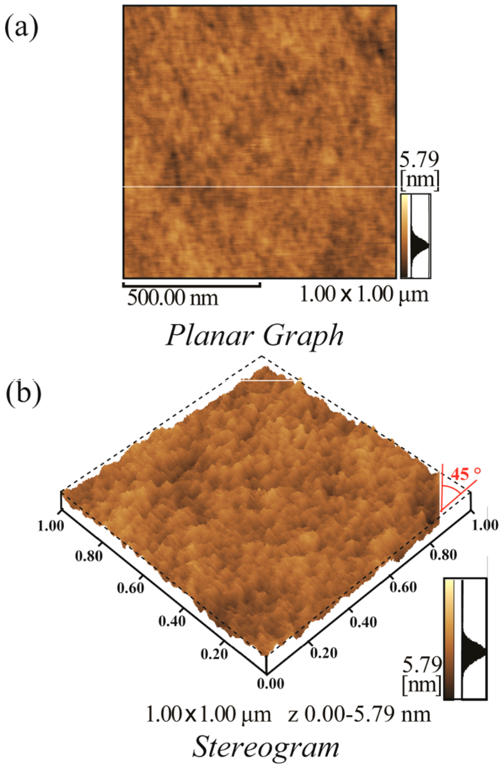


Figure 10. AFM images of a **Si-PFCB** film (thickness of 170.2 nm) on a silicon wafer. (a) Planar graph and (b) stereogram (45°).

provided a new way to prepare cross-linked organosiloxanes, during which the cross-linking was carried out only upon heating, while in the traditional procedures the cross-linking required catalysts or initiators.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The GPC curve and MALDI-TOF-MS Spectrometry of the polymer, NMR Spectra of precursor 3, and the polymer. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: qiangfang@mail.sioc.ac.cn. Fax: +86 21 5492 5337. Tel: +86 21 5492 5337.

Author Contributions

†C.Y. and J.W. contributed equally.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial supports from Ministry of Science and Technology of China (2011ZX02703 and 2015CB931900) and the Natural Science Foundation of China (NSFC, No. 21374131) are gratefully acknowledged. Q.F. thanks Professor Ping Yao in Fudan University for her kind help in the measurement of MALDI-TOF-MS Spectrometry.

■ REFERENCES

(1) (a) Yang, J.; Liu, S.; Zhu, F.; Huang, Y.; Li, B.; Zhang, L. *J. Polym. Sci., Polym. Chem.* **2011**, *49*, 381. (b) de Theije, F. K.; Balkenende, A. R.; Verheijen, M. A.; Baklanov, M. R.; Mogilnikov, K. P.; Furukawa, Y. *J. Phys. Chem. B* **2003**, *107*, 4280.

(2) Volksen, W.; Miller, R. D.; Dubois, G. *Chem. Rev.* **2010**, *110*, 56.

(3) (a) Larsen, G.; Lotero, E.; Marquez, M. *J. Phys. Chem. B* **2000**, *104*, 4840. (b) He, F.; Yuan, C.; Li, K.; Diao, S.; Jin, K.; Wang, J.; Tong, J.; Ma, J.; Fang, Q. *RSC Adv.* **2013**, *3*, 23128.

(4) Morgen, M.; Ryan, E. T.; Zhao, J.; Hu, C.; Cho, T.; Ho, P. S. *Annu. Rev. Mater. Sci.* **2000**, *30*, 645.

(5) Zhao, G.; Ishizaka, T.; Kasai, H.; Hasegawa, M.; Furukawa, T.; Nakanishi, H.; Oikawa, H. *Chem. Mater.* **2009**, *21*, 419.

(6) Martin, S. J.; Godschalx, J. P.; Mills, M. E.; Shaffer, E. O., II.; Townsend, P. H. *Adv. Mater.* **2000**, *12*, 1769.

(7) Huang, Q. R.; Kim, H. C.; Huang, E.; Mecerreyes, D.; Hedrick, J. L.; Volksen, W.; Frank, C. W.; Miller, R. D. *Macromolecules* **2003**, *36*, 7661.

(8) Eslava, S.; Urrutia, J.; Busawon, A. N.; Baklanov, M. R.; Iacopi, F.; Aldea, S.; Maex, K.; Martens, J. A.; Kirschhock, C. E. A. *J. Am. Chem. Soc.* **2008**, *130*, 17528.

(9) Yuan, C.; Jin, K.; Li, K.; Diao, S.; Tong, J.; Fang, Q. *Adv. Mater.* **2013**, *25*, 4875.

(10) Maier, G. *Prog. Polym. Sci.* **2001**, *26*, 3.

(11) Long, T. M.; Swager, T. M. *J. Am. Chem. Soc.* **2003**, *125*, 14113.

(12) Tsuchiya, K.; Ishii, H.; Shibasaki, Y.; Ando, S.; Ueda, M. *Macromolecules* **2004**, *37*, 4794.

(13) Tsuchiya, K.; Shibasaki, Y.; Aoyagi, M.; Ueda, M. *Macromolecules* **2006**, *39*, 3964.

(14) Huang, Y.; Economy, J. *Macromolecules* **2006**, *39*, 1850.

(15) Chen, Y. W.; Wang, W. C.; Yu, W. H.; Kang, E. T.; Neoh, K. G.; Vora, R. H.; Ong, C. K.; Chen, L. F. *J. Mater. Chem.* **2004**, *14*, 1406.

(16) Ro, H. W.; Char, K.; Jeon, E.; Kim, H. J.; Kwon, D.; Lee, H. J.; Lee, J. K.; Rhee, H. W.; Soles, C.; Yoon, D. Y. *Adv. Mater.* **2007**, *19*, 705.

(17) Rathore, J. S.; Interrante, L. V.; Dubois, G. *Adv. Funct. Mater.* **2008**, *18*, 4022.

(18) Farrell, R.; Goshal, T.; Cvelbar, U.; Petkov, N.; Morris, M. A. *ECS Interface* **2011**, *20* (Winter), 39.

(19) Murotani, E.; Lee, J.; Chatzichristidi, M.; Zakhidov, A. A.; Taylor, P. G.; Schwartz, E. L.; Malliaras, G. G.; Ober, C. K. *ACS Appl. Mater. Interfaces* **2009**, *1*, 2363.

(20) Liu, X.; Li, Y. L.; Hou, F. *J. Am. Ceram. Soc.* **2009**, *92*, 49.

(21) Iacono, S. T.; Budy, S. M.; Jin, J.; Smith, D. W., Jr. *J. Polym. Sci., Polym. Chem.* **2007**, *45*, 5705.

(22) Case, C. B.; Case, C. J.; Kornblit, A.; Mills, M. E.; Castillo, D.; Liu, R. *Mater. Res. Soc. Symp. Proc.* **1997**, *443*, 177.

(23) Rizzo, J.; Harris, F. W. *Polymer* **2000**, *41*, 5125.

(24) Bychkova, A. A.; Soskov, F. V.; Demchenko, A. I.; Storozhen, P. A.; Muzafarov, A. M. *Russ. Chem. Bull.* **2011**, *60*, 2384.

(25) Park, J.; Oh, J.; Creager, S. E.; Smith, D. W., Jr *Chem. Commun.* **2012**, *48*, 8225.

(26) (a) Andrew, T. L.; Swager, T. M. *Macromolecules* **2011**, *44*, 2276. (b) Ghim, J.; Lee, D. S.; Shin, B. G.; Vak, D.; Yi, D. K.; Kim, M. J.; Shim, H. S.; Kim, J. J.; Kim, D. Y. *Macromolecules* **2004**, *37*, 5724.